The Interfacial Tension between Liquid Sulfur and Water

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Synopsis

The authors determined the interfacial tension between liquid sulfur and water, and the effects of acid and surface active agents were observed.

The drop weight volume method was previously adopted to make a rough estimate of the value of the interfacial tension. The result was put to an accurate measurement by means of the capillary depression method.

The observed values are summarized and represented by the following equations:

$$\gamma_{S\text{-}H_2O} = 70.99 - 0.1329t \quad (110\sim160°C)$$
$$\gamma_{S\text{-}H_2O} = 57.25 - 0.0470t \quad (160\sim180°C)$$

where $\gamma_{S\text{-}H_2O}$ is the interfacial tension between liquid sulfur and water in dyne/cm and t the temperature in °C.

It was recognized that the interfacial tension was increased by the addition of surfuric acid in the water phase.

The effect of the surface active agent showed an abrupt change in the interfacial tension which is considered to be corresponded to the characteristic concentration of agent.

I. Introduction

In the previous work[1], the authors determined the surface tension of liquid sulfur in nitrogen atmosphere. Further illustrations of the interfacial phenomena in the extraction of sulfur from ore by means of the autoclaving method are associated with the interfacial tension between liquid sulfur and water.

From this point of view, the authors carried out the measurement as follows:

First the drop weight volume method was adopted which is expedient and rapid in procedure with small quantities of sample. From the result obtained, a suitable bore of capillary was chosen for the method of capillary depression. In this way, the temperature dependence of the interfacial tension was accurately measured in the range of temperature from 120 to 180°C under saturated vapor pressure of water.

The experimental procedure and results are described in the following section.

II. Experimental

1. Sample

Pure sulfur prepared by R. F. Bacon and R. Fanelli's method[2] was used. The conductivity water was obtained by treating water with anion and cation exchanger of Amberlite IR-120 and IR-410.

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(1) K. Ono and T. Matsushima, Sci. Rep. RITU, **A9** (1957), 307.

(2) R. F. Bacon and R. Fanelli, Ind. Eng. Chem., **34** (1942), 1043.

2. Effective Density

The effective density taken between liquid sulfur and water was necessary for the calculation of the interfacial tension. No measurement was done for this value. If it were assumed that the mutual solubility of two liquids is not present on the interface, the effective density would be led from the difference between the density of liquid sulfur and that of water.

The density of pure sulfur was chosen from previous works[3][4][5], and that of water from physical table[6].

These differences are found in Fig. 1 versus temperatures.

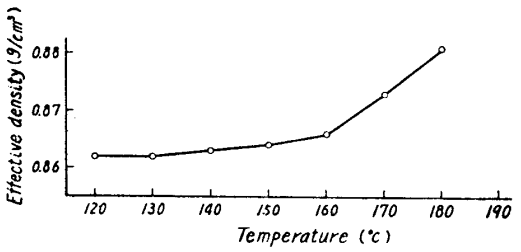

Fig. 1. Relation between temperature and effective density.

3. Preliminary experiment on the interfacial tension by the drop weight volume method

(a) Experimental apparatus and procedure: In this experiment, the measurements were always carried out under saturated vapor pressure of water increasing from 2 to 10 kg/cm^2 and at temperature raising from 120 to 180°C. The apparatus made of hard SB glass is shown in Fig. 2. The vertical tip for a drop formation of liquid sulfur from the reservoir (B) was fixed in the center of the reservoir (A).

First suitable quantitity of solid sulfur grains were put in (B). The water was introduced in (A) through the stainless steel needle valve at the end of the path of b. When the water was completely fulfilled in (A), the excess water was carefully exausted in (B) through capillary tube.

After conditioning at constant temperature, a drop of liquid sulfur was formed and dropped down from the tip, while the operation was carried out by leaking water from a regulated needle valve on b. The pressure required to form a droplet was improved by saturated vapor pressure of water derived in (B).

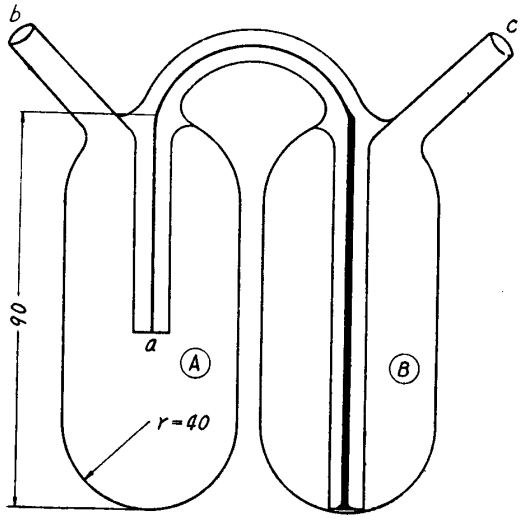

Fig. 2. Experimental apparatus of drop weight volume method.

A Reservoir of droplets
B Reservoir of sample
a Tip
b, *c* To needle valve

The number of droplets was counted and the total weight of sulfur was weighed after experiment.

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(3) T. Matsushima, Res. Inst. Min. Dress. and Met., **11** (1955), 169.
(4) T. Shirai, J. Chem. Soc. (Japan) **72** (1951), 696.
(5) A. M. Kellas, J. Chem. Soc., **113** (1918), 903.
(6) K. Shiba, *Tables of Physical Constants* (1947).

(b) Experimental results: After experiments, the interfacial tension was calculated according to Table 1 by the following equation:

$$\gamma_{S\text{-}HO_2} = \frac{v(\rho_S - \rho_{H_2O})g}{2\pi r}\varphi$$

Table 1. Interfacial tension between liquid sulfur and water. (Drop weight volume method)

No.	Temperature (°C)	Total weight of sulfur (g) w	Numbers of droplets n	Volme of a droplet (cc) $v=w/\rho_S \cdot n$	$r/v^{\frac{1}{3}}$	φ *	$\gamma' = \frac{v(\rho_S-\rho_{H_2O})g}{2\pi r}$	Interfacial tension (dyne/cm) $\gamma=\gamma'\varphi$
1	120	9.4573	335	0.015_6	0.19_2	1.26	43.5	54.8
2	120	9.8457	343	0.015_2	0.19_2	1.26	44.3	55.8
								(Mean)55.3
3	125	7.9000	278	0.015_8	0.19_2	1.26	44.1	55.6
4	125	10.0053	367	0.015_0	0.19_5	1.27	41.8	53.1
								(Mean)54.4
5	140	3.1867	123	0.014_5	0.19_8	1.27	40.5	51.4

* Extrapolated value from Harkins and Brown's Table

** Inside radius of capillary r = 0.0482 cm

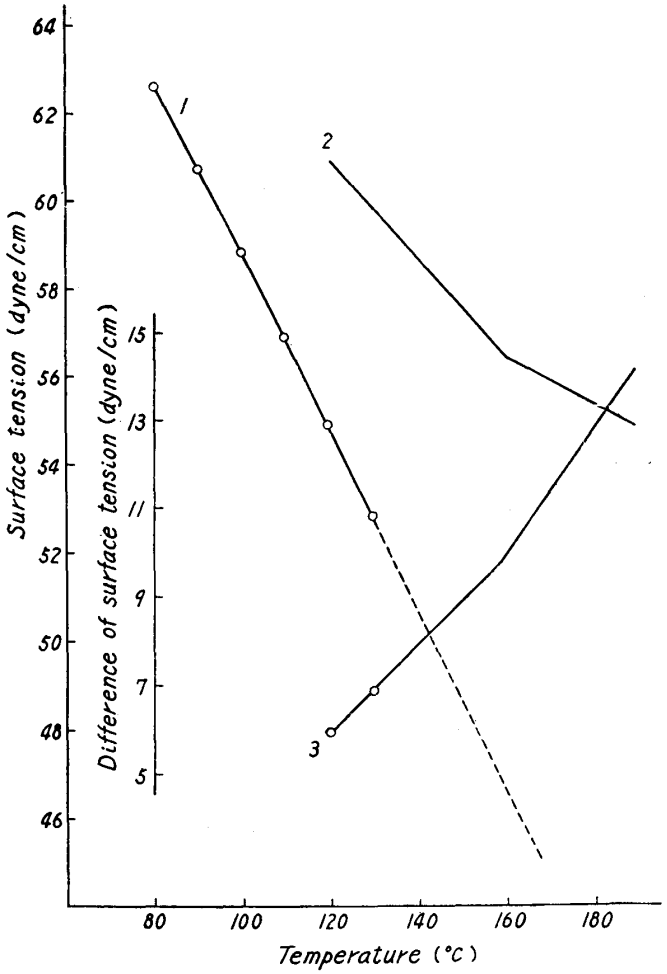

Fig. 3. Surface tension of water and liquid sulfur.
1. Surface tension of water
2. Surface tension of liquid sulfur
3. Difference of surface tension between liquid sulfur and water

where the interfacial tension $\gamma_{S\text{-}H_2O}$ is led from a volume of droplet v, effective density $\rho_S - \rho_{H_2O}$, radius of capillary r, gravity constant g (980.1 cm/sec^2 at Sendai), and the reciprocal number of Harkins and Brown's caribration factor φ.

The results show that the interfacial tension between liquid sulfur and water takes remarkably higher value than simple difference of the surface tension between liquid sulfur and water. For comparison, this differnece is represented in Fig. 3 versus temperature.

On the other hand, the observed ratio of $r/v^{\frac{1}{3}}$ in Table 1 shows that the radius of tip was not suitable. Then the interfacial tension was calculated by the extrapolated value from Harkins and Brown's table. This table identically points out the factor for which it is usually

best to use the tip such as the ratio $r/v^{\frac{1}{3}}$ between 0.759 and 0.95. The experiment was not done with other suitable tip, because only one apparatus was suitable for the maximum pressure of 4.5~5 kg/cm^2. This was not satisfactory for measuring the wide temperature range under high pressure, but the results show that the temperature dependence of the interfacial tension was considered to be decreased in the temperature rising.

4. The interfacial tension by the height of capillary depression method

(a) Experimental apparatus and procedure: The experiments were performed fairly by this method with the apparatus shown in Fig. 4. It was pointed out from the result of the drop weight volume method, that the liquid sulfur was depressed in the capillary tube where a distinct formation of the droplet occurred in the inside bore of the tip. A suitable selection of the radious of capillary could be made from the above result. Its length, however, was defined by the uniformity of temperature in an electric oven.

The apparatus was made of SB hard glass and annealed to remove the stress and strain. It was used after 40 kg/cm^2 pressure test at room temperature. The critical condition of the apparatus was about 15 kg/cm^2 at 180°C in measurement.

After an apparatus was aged by sulfuric acid-dichromate mixture, it was washed and dried. After 160g of liquid sulfur was poured into a preheated vessel, it was solidified and 60 g of water was added. Then the tip of the tube was sealed with the guage with Valqua packing plate.

An electric oven was used as heating source and temperature was automatically regulated and recorded at ±0.2°C.

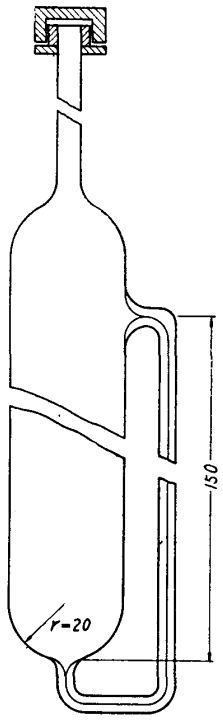

Fig. 4. Experimental apparatus of height of capillary depression method.

The conditioning of two liquids was done in a neighborhood of the melting point of liquid sulfur. The height of capillary depression was read by the cathetometer within an accuracy of ±1/20 mm.

As a result, the interfacial tension was calculated on an assumption that the interfacial contact angle of two liquids on glass wall was 180° from liquid sulfur to water phase.

(b) Experimental results: The experimental results are summarised in Table 2, showing the effect of temperature. For illustration, the relation between the interfacial tension and temperature are shown in Fig. 5. In this figure, the inclination of temperature dependence of the interfacial tension is broken up above 160°C, at which its tendency was similarly observed in the previous work[1] on the surface tension of liquid sulfur.

Table 2. Interfacial tension between liquid sulfur and water (Height of capillary depression method)

Temperature (°C)	Interfacial tension (dyne/cm)	Temperature (°C)	Interfacial tension (dyne/cm)
119.5	55.07	120	55.13
126.5	54.09	128	54.08
133	53.27	131	53.50
140.5	52.42	138	52.62
149.5	51.20	146.5	51.50
156.5	50.25	150	50.93
160	49.79	154.8	50.41
161.5	49.68	158	49.98
164	49.52	160	49.65
166.8	49.36	166	49.42
168	49.25	170	49.22
176	48.99	179.5	48.93
177	48.93		
178.5	48.85		
Conditioning time (min)	1185		3015
Measuring time (min)	1650		2670
pH of water after measurement	2.10		2.21
Radius of capillary(cm)	0.0201		0.0276

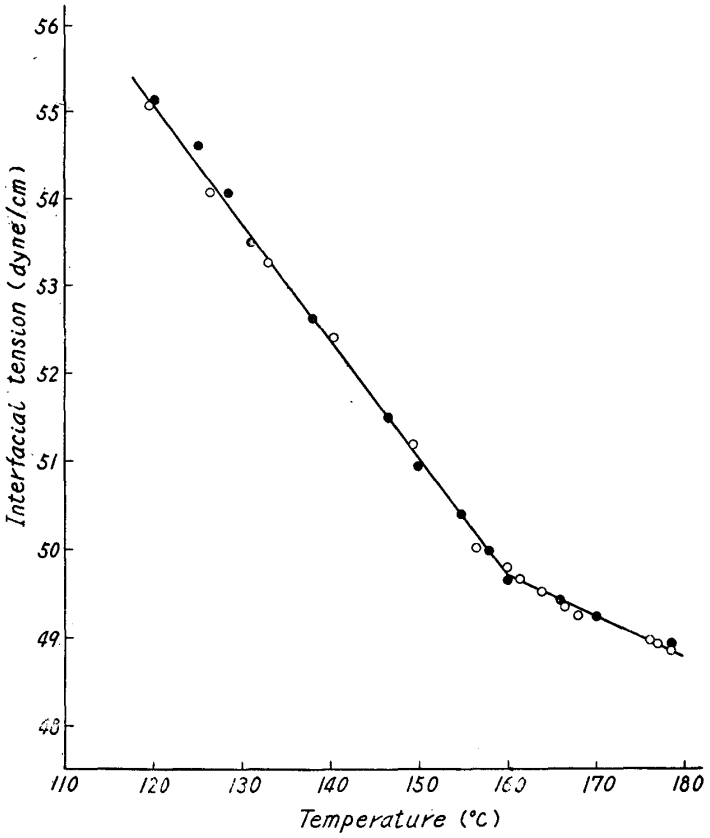

Fig. 5. Interfacial tension between liquid sulfur and water.

○ r = 0.0201 cm
● r = 0.0276 cm

On the other hand, the chemical reaction between liquid sulfur and water should be considered. However various conditions of the measurement showed no effect on the results. It is considered that it was done in an equilibrium state.

After experiments, hydrogen ion concentration of water always existed in the range of 2.1~2.2 of pH value.

5. Effect of acid in water on the interfacial tension

From the above experiment, water was acidified, which is considered to be a result of the chemical reaction between liquid sulfur and water. On the other hand, it has been empirically discussed as the effect of acidity of water, while the operation was sometimes carried out in pH from 1 to 3 by an autoclaving method. No conclusion was formed on this problem. From this fact, the authors determined qualitatively the effect of acidity on the interfacial tension.

The measurement was made with an aqueous solution of sulfuric acid. The experimental results are shown in Fig. 6, where the calculation was made on an assumption of the effective density, which is equal to the difference between two densities of pure sulfur and pure water.

It was considered that the interfacial tension of liquid sulfur with 0.1N H_2SO_4 solution behaved in the manner similar to that of liquid sulfur with water, but when the concentration of acid was increased to 1.5N, was seen to take a high value.

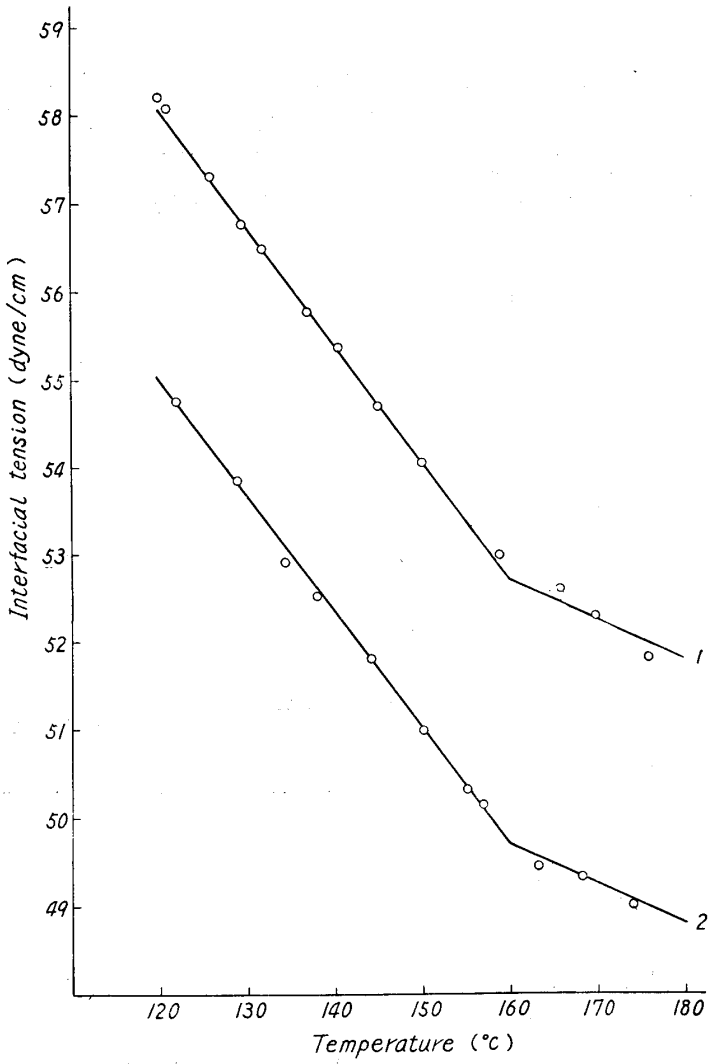

Fig. 6. Effect of acid on interfacial tension
1. 1.5N H_2SO_4
2. 0.1N H_2SO_4

6. Effects of surface active agents on the interfacial tension

When it was previously observed that the surface active agent improved the extraction of sulfur in an autoclaving method,[8] it was inferred that it improved the coagulation of liquid sulfur. This fact was of interest in considering the change

(8) T. Matsushima, Res. Inst. Min. Dress. and Met., **9** (1953), 277. C.A. **49** (1955), 13607g.

of the interfacial phenomena between liquid sulfur and aqueous solution of surface active agent.

From this point of view, the authors determined the effects of agents on the interfacial tension.

Two anionic agents of ester of sodium lauryl sulfate (Surfactant A) and sodium alkylnaphthalensulfonate (Surfactant B), and non-ionic agent of polyoxyethylen sorbitan oleate (Surfactant C) were used. These agents were apparently stable thermally and accompanied no chemical reaction with sulfur in observed range of the temperature. The purity of surfactant A was of chemical grade and others were of commercial grade.

The concentration of aqueous solution was chosen from the comparison with that of the characteristic properties such as surface tension, which is reliable in critical micelle concentration. For this purpose, the surface tension is given in Fig. 7 with various concentrations of agent.

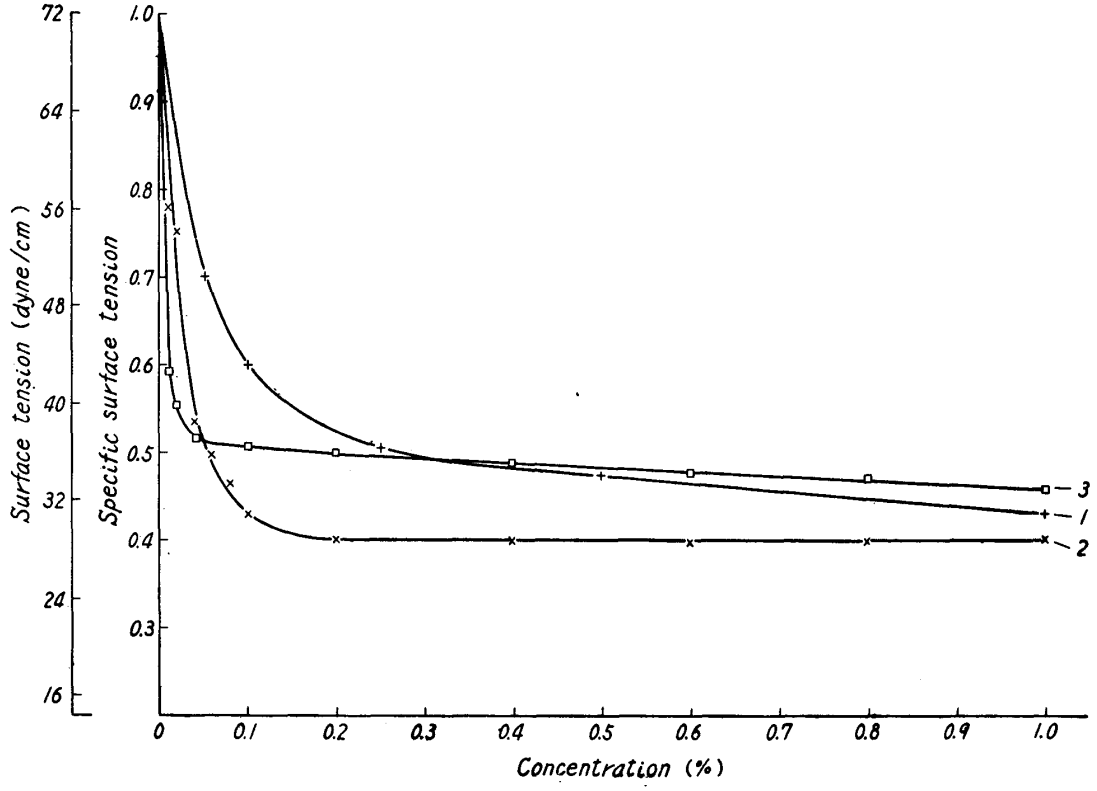

Fig. 7. Physical properties of surface active agents (Surface tension).

Anionic agent { 1 Sodium lauryl sulfate
2 Sodium alkylnaphthalensulfonate
Non-ionic agent { 3 Polyoxyethylene sorbitan oleate
Temperature: 25±0.1°C

(a) Effect of Surfactant A: The experimental results are shown in Fig. 8. In these results, calculated interfacial tension was assumed to be the effective density taken in the above section. The interfacial tension was lower than that between liquid sulfur and water, but it increased with rise in temperature and the decrease in concentration of agent.

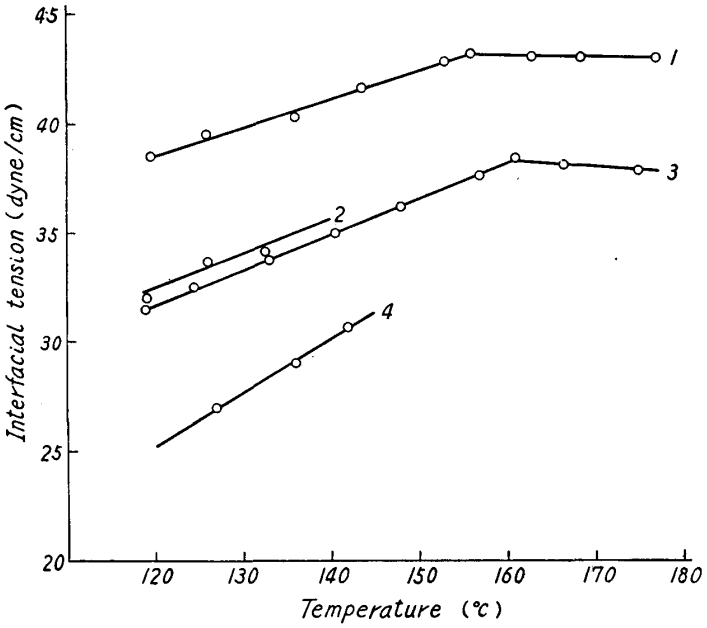

Fig. 8. Effect of sodium lauryl sulfate.

Concentration
1. 0.10%
2. 0.20%
3. 0.34%
4. 0.50%

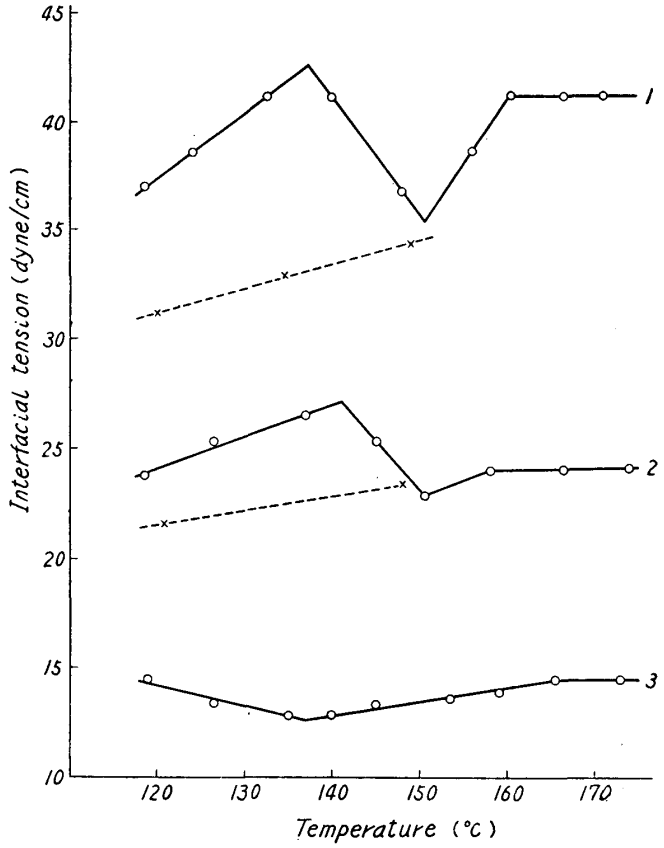

Fig. 9. Effect of alkylnaphthalensulfonate.

Concentration
1. 0.1%
2. 0.2%
3. 0.4%

—○— Temperature rising
--×-- Temperature falling

(b) Effect of Surfactant B: Surfactant B shows an irregular change in the interfacial tension, as shown in Fig. 9, with rise in temperature. In a measurement made with falling temperature, it took lower values, which are shown in hatched line in Fig. 9. This is apparently an extrapolation from the result of high temperature.

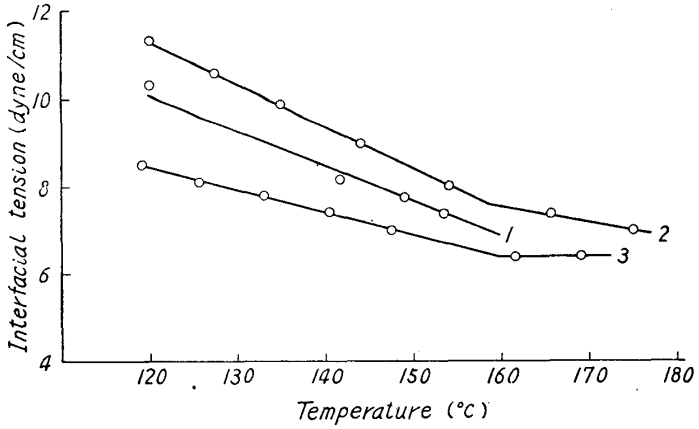

Fig. 10. Effect of polyoxyethylen solbitan oleate.
Concentration { 1. 0.025%
2. 0.078%
3. 0.29 %

(c) Effect of Surfactant C: Surfactant C behaved like liquid sulfur with pure water with rise in temperature, and the results shown in Fig. 10 are the lowerest of these three agents.

For illustration, the relation between the interfacial tension and the concentration of agent was taken from the isothermal result obtained at 120°C in Fig. 11. An abrupt change of the interfacial tension was considered to correspond to the characteristic concentration of agent.

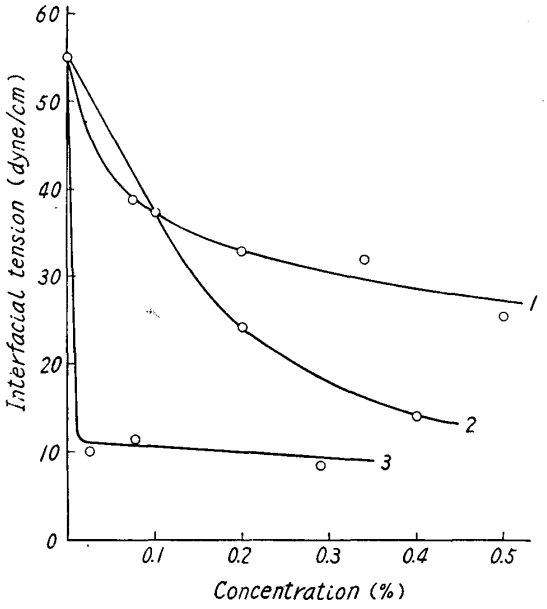

Fig. 11. Relation between interfacial tension and concentration of agent (120°C).
1. Sodium lauryl sulfate
2. Alkylnaphthalensulfonate
3. Polyoxyethylen solbitan oleate

III. Conclusion

The authors determined the interfacial tension between liquid sulfur and water by the method of the drop weight volume and that of the height of capillary depression. Both results agreed in the order of value, but an accurate measurement was made by the latter method. The observed values versus temperatures are summarized as follows:

$$\gamma_{S\text{-}H_2O} = 70.99 - 0.1329\,t \qquad (120\sim160°C)$$

$$\gamma_{S\text{-}H_2O} = 57.25 - 0.0470\,t \qquad (160\sim180°C)$$

where $\gamma_{S\text{-}H_2O}$ is the interfacial tension between liquid sulfur and water in dyne/cm and t the temperature in °C. The change of the temperature dependence above 160°C was considered to be caused by the polymerization of sulfur. In the previous work, E. Delpiano[9] determined the interfacial tension to be 54.5 dyne/cm at 130°C

(9) E. Delpiano, Minerals (Chile) 9 No. 47 (1954), 55. C. A. **50** (1956), 9823a.

by the drop weight method. This is in a good agreement with the value calculated from the above equation at the same temperature except the authors' result by the drop weight volume method.

These results show that the interfacial tension between liquid sulfur and water considerably takes higher value than a simple difference of the surface tension between liquid sulfur and water.

In the above experiment, water was always acidified in pH 2.1~2.2 after measurement. It was considered to be caused by the chemical reaction between liquid sulfur and water. Then, the effect of acidity of solution was measured by the aqueous solution of sulfuric acid. It was recognized that the interfacial tension was increased by the addition of an acid, and its temperature dependence was similar to the result between liquid sulfur and water.

The effects of the surface active agents were measured. The experimental result show an abrupt change in the interfacial tension near the characteristic concentration of agent. From this point of view, it was considered that its effect of lowering the interfacial tension between liquid sulfur and water was related to an improvement in the coagulation of liquid sulfur in an autoclaving method.

In conclusion the authors wish to express their hearty thanks to Asst. Prof. T. Okabe for his guidance throughout high pressure technique. The present work was partially supported by the fund in aid of Scientific Research of the Ministry of Education.